High Efficiency Segmented Thermoelectric Unicouples

Thierry Caillat, Alex Borshchevsky, Jeff Snyder, and Jean-Pierre Fleurial

Jet Propulsion laboratory/California Institute of Technology, Pasadena, CA 91109

818-354-0407; thierry.caillat@jpl.nasa.gov

Abstract. A new version of a segmented thermoelectric unicouple incorporating advanced thermoelectric materials with superior thermoelectric figures of merit has been recently proposed and is currently being developed at the Jet Propulsion Laboratory. The advanced segmented unicouple currently being developed would operate over a 300 to 975K temperature difference and the predicted efficiency is about 15%. There has been recently a growing interest for thermoelectric power generation using various waste heat sources such as the combustion of solid waste, geothermal energy, power plants, automobile, and other industrial heat-generating processes. Hot-side temperatures ranging from 370 to 1000K have been reported in the literature for some of these potential applications. Although the segmented unicouple currently being developed is expected to operate at a hot-side temperature of 975K, the segmentation can be adjusted to accommodate various hot-side temperatures depending on the specific application. This paper illustrates various segmentation options corresponding to hot-side temperatures ranging from 675 to 975K. The predicted efficiency and characteristics of the corresponding unicouples are described.

INTRODUCTION

A new version of a segmented thermoelectric unicouple incorporating advanced thermoelectric materials with superior thermoelectric figures of merit has been recently proposed and described (Caillat, 1998 and 1999a) (Fleurial, 1997a and 1997b). This segmented unicouple, under development at the Jet Propulsion Laboratory (JPL), contains a combination of state-of-the-art thermoelectric materials based on Bi_2Te_3 and novel p-type Zn_4Sb_3, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys developed at JPL. To achieve high thermal to electrical efficiency, it is desirable to operate thermoelectric generator devices over large temperature differences and also to maximize the thermoelectric performance of the materials used to build the devices. The advanced segmented unicouple currently being developed would operate over a 300 to 975K temperature difference and the segmenting of the n- and p-legs into several sections made of different materials would increase the average thermoelectric figure of merit of the legs compared to using a single material per leg or/and state-of-the-art thermoelectric materials. In the current version, the predicted efficiency would be about 15%. Despite their relatively low efficiency, thermoelectric generator devices are used in various industrial applications because of their high reliability, low maintenance and long life, in particular when considering harsh environments. The most common applications are for cathodic protection, data acquisition and telecommunications. More recently, there is a growing interest for waste heat recovery power generation, using various heat sources such as the combustion of solid waste, geothermal energy, power plants, and other industrial heat-generating processes. Hot-side temperatures ranging from 370 to 1000K have been reported in the literature. Because of the need for cleaner, more efficient cars, car manufacturers worldwide have also expressed some interest for using waste heat generated by the vehicle exhaust to replace or supplement the alternator. If successful, more power would become available to the wheels and the fuel consumption would decrease. According to some car manufacturers, the available temperature range would be from 475 to 675K. There is therefore a variety of potential applications for advanced thermoelectric generators with a diversity of hot-side temperatures. Although the segmented unicouple currently being developed is expected to operate at a hot-side temperature of 975K, the segmentation can be adjusted to accommodate various hot-side temperatures depending on the specific application. This paper illustrates various segmentation options and the predicted efficiency and characteristics of the corresponding unicouples.

SEGMENTED UNICOUPLE VERSION UNDER DEVELOPEMENT

The segmented unicouple under development incorporates a combination of state-of-the-art thermoelectric materials and novel p-type Zn_4Sb_3, p-type $CeFe_4Sb_{12}$-based alloys and n-type $CoSb_3$-based alloys developed at JPL. In a segmented unicouple as depicted in Figure 1, each section has the same current and heat flow as the other segments in the same leg. Thus in order to maintain the desired temperature profile (i.e. keeping the interface temperatures at their desired level) the geometry of the legs must be optimized. Specifically, the relative lengths of each segment in a leg must be adjusted, primarily due to differences in thermal conductivity, to achieve the desired temperature gradient across each material. The ratio of the cross sectional area between the n-type and p-type legs must also be optimized to account for any difference in electrical and thermal conductivity of the two legs. A semi-analytical approach that includes smaller effects such as the Peltier and Thompson contributions and contact resistance in order to optimize and calculate the expected properties of the device has been used to solve the problem (Swanson, 1961). For each segment, the thermoelectric properties are averaged for the temperature range it is used. At each junction (cold, hot, or interface between two segments), the relative lengths of the segments are adjusted to ensure heat energy balance at the interface. Without any contact resistance between segments, the efficiency is not affected by the overall length of the device; only the relative length of each segment needs to be optimized. The total resistance and power output, however, does depend on the overall length and cross sectional area of the device. The calculated optimized thermoelectric efficiency is about 15% with the hot junction at 975K and the cold junction near room temperature. The optimal geometry is illustrated in Figure 1.

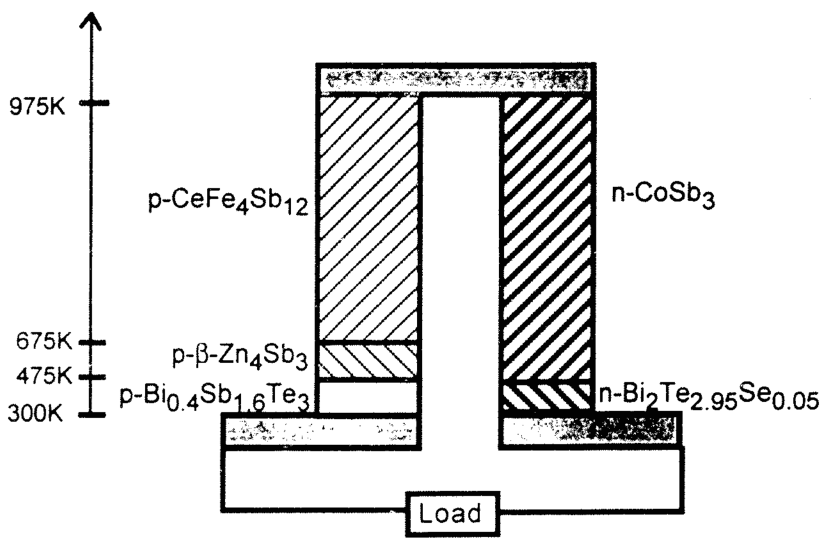

FIGURE 1. Illustration of the advanced unicouple incorporating new high performance thermoelectric materials. The relative lengths of each segment and the cross-sectional areas for the p- and n-legs are drawn to scale. The calculated thermoelectric efficiency is 15%.

High contact resistance between the thermoelectric segments can dramatically reduce the efficiency of a generator. Calculations show that a low contact resistance, less than about 20 $\mu\Omega cm^2$, is required to keep the efficiency from being significantly degraded by the contact resistance. Techniques and materials have been developed to bond the different segments of the unicouple together and also the lower and upper segments to the interconnects (Caillat, 1999b). Electrical contact resistance lower than 5 $\mu\Omega cm^2$ have been obtained for each of the junctions at its projected operating temperature. The unicouple illustrated in Figure 1 has been built and thermal and electrical tests are in progress (Caillat, 1999b). As previously mentioned, the hot-side temperature may vary depending on the specific application and this would require a different optimization of the geometry of the legs. However, the bonding techniques an materials developed for the version of the unicouple operating at a hot-side temperature of 975K could be apply for the fabrication of unicouples operating at lower hot-side temperatures.

POSSIBLE SEGMENTATION VARIATIONS

The maximum hot-side operating temperature of the segmented unicouple is limited to 975K because of the limited temperature stability of the thermoelectric materials used for the upper segments above about 1075K. Efforts are underway to develop skutterudite based materials which could operate at significantly higher temperatures. Preliminary results obtained on arsenide and phosphide skutterudites show that these materials are more refractory than their antimonide analogs and therefore could potentially used at higher temperatures. Efforts are underway to fully assess the potential of some of these materials for thermoelectric applications in particular for use tin segmented unicouples. Increasing the hot-side temperature would result in an increase of the thermoelectric efficiency of the unicouple as illustrated in Figure 2 which shows the variations of the thermoelectric efficiency as a function of the hot-side temperature of the unicouple for two different cold-side temperatures: 300 and 500K. Even if the hot-side temperature is lowered to 700K while the cold-side temperature is maintained at 300K, efficiency about 10% can still be achieved.

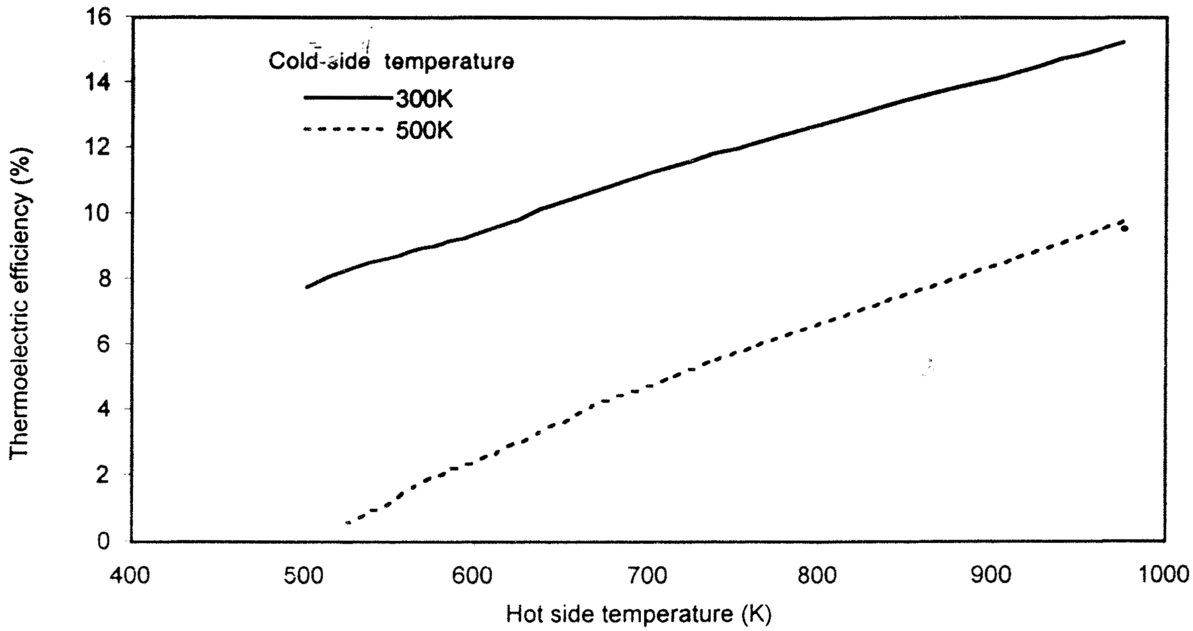

FIGURE 2. Thermal to electrical conversion efficiency as a function of temperature for two different cold-side temperatures : 300 and 500K.

To illustrate the impact of varying the hot-side temperature on the segmented unicouple geometry, some of the thermal, electrical and geometrical properties of the unicouple have been calculated for three different hot-side temperatures : 975, 775, and 675K and are listed in Table 1. Decreasing the hot-side temperature from 975 to 675K results in a decrease of the efficiency from 15 to about 10%. The relative lengths of the segments and cross-sectional areas of unicouples with hot-side temperature of 775 and 675K are illustrated in Figure 3. Decreasing the hot-side temperature from 975 to 775K results in an increase of the lengths of the two lower segments of the p-legs and all three segments have a much closer length than for the 975K version. This could be an important factor if one needs to fabricate very small legs for example for an application for which a relatively high voltage is required. If the lengths of the segments are too disproportionate, it would be more difficult to scale down the size of the legs. The thermoelectric efficiency decreases only from 15% to about 12% going from a hot-side temperature of 975K to a hot-side temperature of 775K. While both version 1 and 2 unicouples have three segments for the p-leg, the unicouple with a hot-side temperature of 675K would only use two p-type materials, *i.e.* Zn_4Sb_3 and $Bi_{0.4}Sb_{1.6}Te_3$. In this version, the two p-type segments would be about equal in length but the p-leg would possess a much lower average thermal conductivity than the n-leg which would result in a much smaller cross sectional area, about 50% smaller than that of the p-type. Much of the difference of the thermal conductivity for the n-leg is attributed to the relative large thermal conductivity of n-$CoSb_3$ (~40mW/cmK) compared to the other materials (~12 mW/cmK). Efforts are currently underway to develop alloys based on $CoSb_3$ which would have similar thermoelectric figure of merit in the temperature range of interest but much lower thermal conductivity. Such materials could be used to replace n-$CoSb_3$ in the segmented unicouple, resulting in a more proportionate geometry for the p- and n-legs with respect to their relative cross-sectional areas.

TABLE 1. Some properties of three segmented unicouples with a hot-side temperature of 975, 775, and 675K.

Property	Version 1	Version 2	Version 3
Hot side temperature (K)	975	775	675
Cold-side temperature (K)	300	300	300
n/p cross sectional area ratio (%)	84	67	48
Power output (Watts)	6.3	2.2	0.8
Current (Amps)	37	19.6	10.24
Efficiency (%)	15.2	12.3	9.8

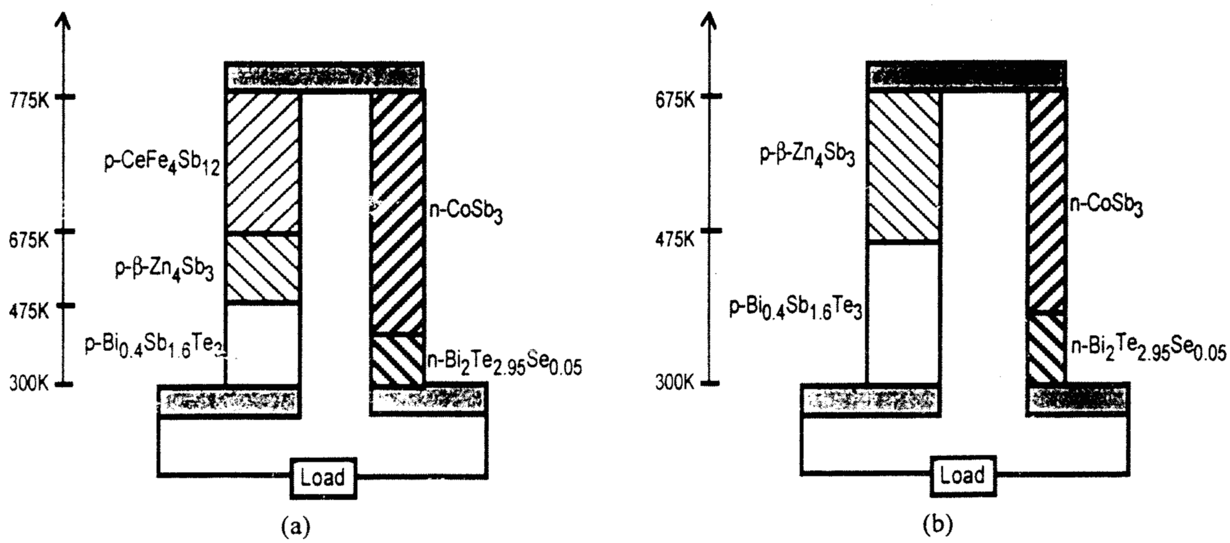

FIGURE 3. Illustrations of two advanced versions of segmented unicouple with a hot-side temperature of a) 775K and b) 675K. The relative lengths of each segment and the cross-sectional areas for the p- and n-legs are drawn to scale.

CONCLUSION

A new version of a segmented thermoelectric unicouple incorporating advanced thermoelectric materials with superior thermoelectric figures of merit is currently under development at JPL. The advanced segmented unicouple would operate over a 300 to 975K temperature difference and the predicted efficiency is about 15%. Techniques and materials have been developed to achieve low electric resistance bonds between the different segments of the unicouple and also between the lower and upper segments to the interconnects Thermal and electrical tests are in progress. Considering the growing interest for waste heat recovery thermoelectric power generation worldwide and the variety of potential heat sources with hot-side temperatures ranging from 370 to 1000K, possible variations of the segmentation to adjust the geometry and optimize the efficiency for a specific hot-side temperature have been described in this paper. Even if the hot-side temperature is decreased to 675K, efficiency values of about 10% can still be achieved. Some adjustments of the segments geometry would be necessary but the techniques and materials developed to date for the version which would operate at a temperature of 975K can be directly used for modified versions of segmented unicouples operating between 675 and 975K.

ACKNOWLEDGMENTS

The work described in this paper was carried out at the Jet Propulsion Laboratory/California Institute of Technology, under contract with the National Aeronautics and Space Administration. This work is supported by the U. S. Defense Advanced Research Projects Agency, Grant No. E748.

REFERENCES

Caillat, T., Borshchevsky, A., and Fleurial, J. -P., in *Proceedings of the 15th Symposium on Space Nuclear Power and Propulsion*, edited by M. S. El-Genk editor, AIP Conference Proceedings 420, New York, USA, 1998, pp. 1647-1651.

Caillat, T., Fleurial, J. -P. , Snyder, G. J., Zoltan, A., Zoltan, D., and Borshchevsky, A., in *Proceedings of the 16th Symposium on Space Nuclear Power and Propulsion*, AIP Conference Proceedings 458, edited by M. S. El-Genk, New York, 1999a, pp. 1403-1408.

Caillat, T., Fleurial, J. -P. , Snyder, G. J., Zoltan, A., Zoltan, D., and Borshchevsky, A., in *Proceeding of 18th International Conference on Thermoelectrics*, edited by Ehrlich, A., IEEE, Piscataway, in press, 1999.

Fleurial, J. -P., A. Borshchevsky, A., and Caillat, T., in *Proceedings of the 1st Conference on Synergistic Power and Propulsion Systems Technology*, edited by M. S. El-Genk, AIP Conference Proceedings 387, American Institute of Physics, New York, 1997a, pp. 293-298.

Fleurial, J. -P., A. Borshchevsky, A., Caillat, T., and Ewell, R., in *Proceedings of the 32nd Intersociety Energy conversion Engineering Conference*, American Institute of Chemical Engineers, New York, 1997b, pp. 1080-1085.

Swanson, B. W., Somers, E. V., and Heike, R. R., *Journal of Heat Transfer*, 77 (1961).